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Thermoelectric properties of bismuth antimony tellurium thin films through bilayer annealing prepared by ion beam sputtering deposition

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ABSTRACT

Bismuth antimony tellurium is one of the most important tellurium-based materials for high-efficient thermoelectric application. In this paper, ion beam sputtering was used to deposit Bi_2Te_3 and Sb_2Te_3 bilayer thin films on borosilicate substrates at room-temperature. Then the bismuth antimony tellurium thin films were synthesized via post thermal treatment of the Bi_2Te_3 and Sb_2Te_3 bilayer thin films. The effect of annealing temperature and compositions on the thermoelectric properties of the thin films was investigated. After the thin films were annealed from 150 °C to 350 °C for 1 h in the high vacuum condition, the Seebeck coefficient changed from a negative sign to a positive sign. The X-ray diffraction results showed that the synthesized tellurium-based thermoelectric thin film exhibited various alloys phases, which contributed different thermoelectricity conductivity to the synthesized thin film. The overall Seebeck coefficient of the synthesized thin film changed from negative sign to positive sign, which was due to the change of the primary phase of the tellurium-based materials at different annealing conditions. Similarly, the thermoelectric properties of the films were also associated with the grown phase. High-quality thin film with the Seebeck coefficient of 240 $\mu V\ K^{-1}$ and the power factor of $2.67 \times 10^{-3}\ Wm^{-1}\ K^{-2}$ showed a single $Bi_{0.5}Sb_{1.5}Te_3$ phase when the Sb/Te thin film sputtering time was 40 min.

1. Introduction

Thermoelectric materials are eco-friendly materials, which can interconvert heat and electric energy directly [1]. Thermo-electric generator based on thermoelectric materials is widely used as a clean, reliable and sustainable energy source [2]. The performance of thermoelectric material is determined by a parameter which is defined as a dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S, σ, T, κ are the Seebeck coefficient, electric conductivity, absolute temperature and thermal conductivity, respectively [3,4]. Bismuth–Antimony–Tellurium is a well-established thermoelectric material that is used in the temperature range of 200–400 K due to its high Seebeck coefficient, good electric conductivity and low thermal conductivity [5–9]. P-type $Bi_{0.5}Sb_{1.5}Te_3$ and n-type $Bi_{1.4}Sb_{0.6}Te_3$ bulk materials have high power factors of $4.0 \times 10^{-3}\ Wm^{-1}\ K^{-2}$, $1.9 \times 10^{-3}\ Wm^{-1}\ K^{-2}$ and ZT of 1.4, 0.3 at room-temperature, respectively. Thin film technique is a good method to improve the thermoelectric properties of thermoelectric materials due to its stronger quantum confinement effect [10,11]. Many studies have been done to fabricate the bismuth antimony tellurium thin film using techniques such as physical vapor deposition or chemical vapor deposition techniques [12–14]. However, neither the Seebeck coefficients nor the conductivity of the thin films prepared by vacuum sputtering method is as good as their bulk material. This is mainly due to the high vapor pressure of Te and the re-evaporation of Te during the preparation [15]. Compared with other techniques, ion beam sputtering deposition (IBSD) is a very attractive technique since it combines a high deposition rate with great versatility in the deposition of thin films by adjusting the target composition and controlling the sputtering energy. In addition, stoichiometric Sb_2Te_3 and Bi_2Te_3 alloy thin films have been obtained by IBSD with fan-shape target in our previous work [16,17]. The quality of the thin films fabricated by IBSD is great and comparable with the best results reported in literature for the same material prepared by other sputtering technologies. In this work, Bi/Te and Sb/Te bilayer thin films were deposited at room temperature by IBSD and P-type $Bi_{0.5}Sb_{1.5}Te_3$ compound thin film was obtained via post thermal treatment of the bilayer. The influence of thermal treatment parameters on fabricating $Bi_{0.5}Sb_{1.5}Te_3$ thin films was studied. The dependence of preparing parameters on the thermoelectric properties of the annealed bismuth antimony tellurium thin films was also investigated.

2. Experimental details

As source materials, two composite targets which were fan-shaped with high purity Sb (99.99%)/Te (99.99%) and Bi (99.99%)/Te (99.99%)

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were fixed in the sputtering sites of the IBSD. The ratio of Sb to Te and Bi to Te was controlled by adjusting the area ratios of the corresponding target plates. The detailed parameters for preparing stoichiometric Sb_2Te_3 and Bi_2Te_3 thin films had been report elsewhere [16,17]. Square soda-lime glasses with a length of 30 mm and thickness of 1.5 mm were used as substrates and were cleaned in acetone, alcohol and deionized water, each for 10 min respectively. The background pressure was 7.0×10^{-4} Pa and the work pressure was 6.1×10^{-2} Pa. A 15 min sputtering cleaning process with a low energy ion beam was performed to remove the contaminants on both the targets and the substrate surfaces prior to film deposition. Plasma energy of 700 keV and beam current of 10 mA were used for sputtering. Firstly, Bi/Te alloy thin films were deposited on the substrates at room-temperature and the deposition time was 30 min. Secondly, the Sb/Te alloy thin films are deposited on the Bi/Te films with the sputtering time of 30 min. Based on our previous research, it had an advantage of improving the thermoelectric properties because the richer Te can be eliminated during the annealing process in vacuum. So the samples were annealed from 150 °C to 350 °C in vacuum for 1 h. The chamber pressure for annealing was less than 8.0×10^{-4} Pa. The effects of the annealing temperature on the properties were investigated. The film annealed at 300 °C has better thermoelectric properties than the others, therefore, all the films with various compositions were prepared with the same annealing temperature of 300 °C. The compositions of the samples were controlled by changing the sputtering time of the Sb/Te thin film while fixing the sputtering time of the Bi/Te thin film to 30 min. The sputtering time of Sb/Te thin film had been set to 10 min, 20 min, 30 min, 40 min and 50 min, respectively. Then the properties of the thin films were studied.

The structure of the thin films was characterized by X-ray diffraction (XRD) technique (D/max2500 Rigaku Corporation) with the conventional θ-2θ mode of the CuK_α radiation ($\lambda = 0.154056$ nm). The thin film thickness was obtained by using a DEKTAK^3 ST surface-profile measurement system. The sheet resistance R_s was determined from a four-point method with a Keithley 2400 current–voltage measurement unit (Keithley Corporation). Electrical conductivity was obtained using $\sigma = (R_s d)^{-1}$. The Seebeck coefficient was measured at room-temperature by a Seebeck coefficient measurement system (SDFP-). The composition ratio and the cross-section view of the thin films were determined by using an energy dispersive X-ray spectroscopy (EDS) microanalysis system (S-4700 Hitachi Corporation).

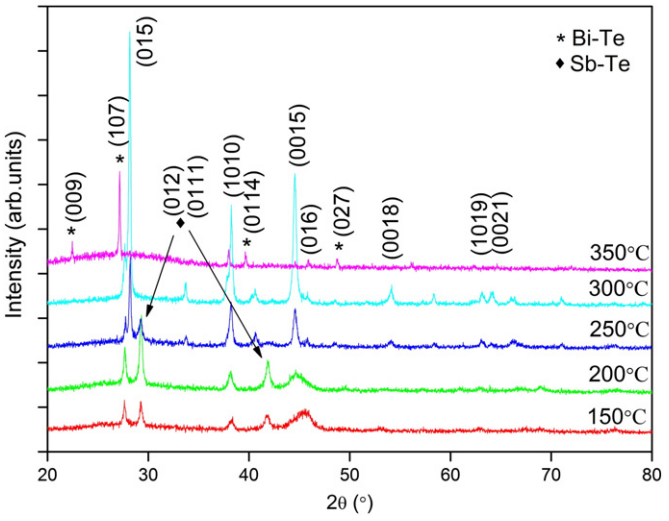

Fig. 1. The XRD patterns of bismuth antimony tellurium thin films as a function of annealing temperature. (Sputtering time: Bi/Te 30 min, Sb/Te 30 min.)

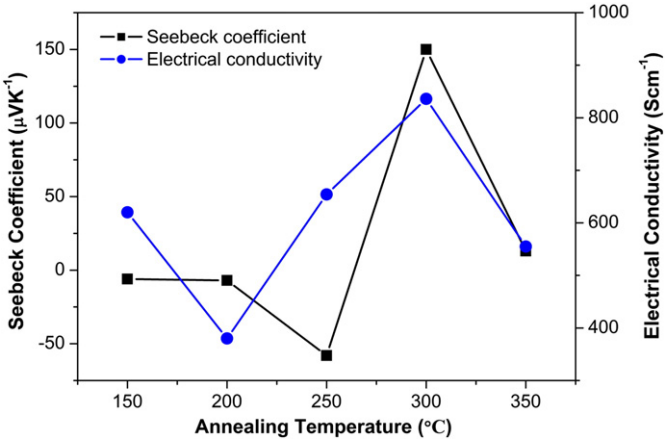

Fig. 2. The Seebeck coefficient and the electrical conductivity of the thin films as a function of the annealing temperature. (Sputtering time: Bi/Te 30 min, Sb/Te 30 min.)

3. Results and discussion

Fig. 1 shows the XRD patterns of bismuth antimony tellurium thin films as a function of annealing temperature. The samples were annealed at 150 °C, 200 °C, 250 °C, 300 °C and 350 °C, respectively. The major diffraction peaks located at 2θ of 28.2°, 38.3° and 44.6° are observed and most peaks of the XRD patterns are related to the $Bi_{0.5}Sb_{1.5}Te_3$ characteristic phase. However, there are also some peaks which are not related to any of the well known bismuth antimony tellurium phase. Instead, they are indexed as Sb–Te and Bi–Te phases at different annealing parameters. When the thin films were annealed at a temperature of 150 °C, the Bi–Te phase is the dominating phase. It is suggested that the Bi–Te compound is easier to be synthesized than other materials containing Sb due to the low melting point of the Bi and Te. The phase transforms to the $Bi_{0.5}Sb_{1.5}Te_3$ and Sb–Te phases when the temperature increased to above 200 °C. With the increase in annealing temperature, the intensity of the peaks related to the $Bi_{0.5}Sb_{1.5}Te_3$ phase, such as (015), (1010) and (0015) which are located at 28.2°, 38.3° and 44.6°, is enhanced and other peaks related to $Bi_{0.5}Sb_{1.5}Te_3$ also increase. Less impurity peaks in the sample can be observed and their intensities are much smaller than the characteristic peaks when the temperature reached 250 °C and 300 °C, which indicates that the $Bi_{0.5}Sb_{1.5}Te_3$ phase is the dominant phase and the thin films have high crystalline quality. However, some peaks related to $Bi_{0.5}Sb_{1.5}Te_3$ disappear when the temperature increases to 350 °C. A phase transition into the Sb–Te + $Bi_{0.5}Sb_{1.5}Te_3$ phase happened and the Sb–Te phase is the major grown phase of the thin films as evident from the XRD pattern shown in Fig. 1. It is speculated that the evaporation of Te and the separation of Bi during annealing can result in the loss of Te and Bi, so the Sb–Te can sufficient synthesize at high temperature.

Fig. 2 shows the Seebeck coefficient and the electrical conductivity of the thin films as a function of the annealing temperatures. It can be found that the Seebeck coefficient increases from -6 μV K^{-1} to -58 μV K^{-1} when the temperatures increased from 100 °C to 250 °C. Then the Seebeck coefficient changed from a negative sign to a positive sign

Table. 1
The element content and thin film thickness as a function of sputtering time by SEM and EDS analyzed.

Sputtering time	10 min	20 min	30 min	40 min	50 min
Bi (%)	42.9	36.5	29.7	10.4	3.5
Sb (%)	9.8	13.6	18.2	31.5	37.9
Te (%)	47.3	49.9	52.1	58.1	58.6
Thickness (nm)	410	510	530	670	750

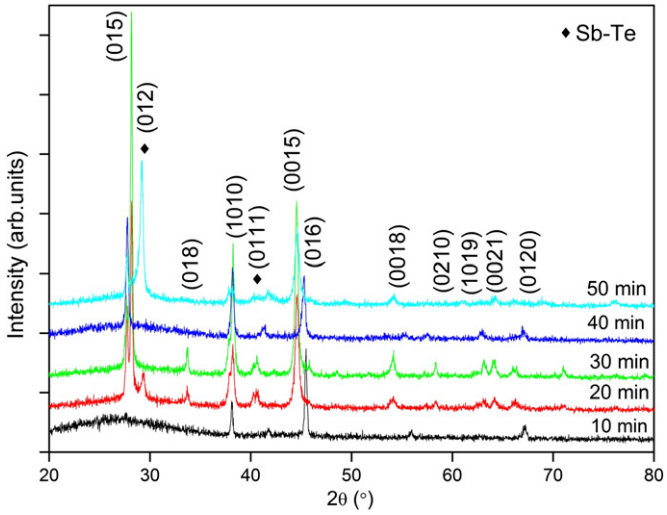

Fig. 3. The XRD patterns as a function of the Sb/Te sputtering time.

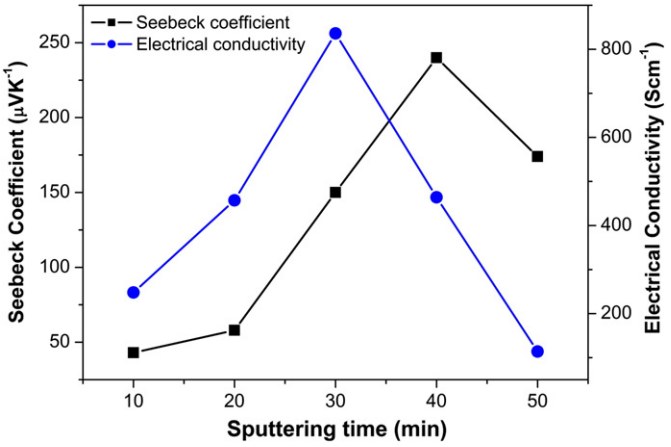

Fig. 5. The Seebeck coefficient and the electrical conductivity of the thin films as a function of the Sb/Te sputtering time.

after the temperature increased to 300 °C and 350 °C. This indicates that the conduction of the thin film changes from N-type to P-type when the annealing temperature increased. With the X-ray diffraction analysis, the change of the thermoelectric type is mainly due to the change of the primary tellurium-based materials at different annealing conditions and the thermoelectric properties of the thin films are associated with the grown phase, so the conversation of the conduction type is mainly due to the increase of the Sb atomic which always results in the p-type conduction. When the films were annealed at low temperature, Bi–Te is the dominant phase and the conductivity of Bi–Te is higher than those of $Bi_{0.5}Sb_{1.5}Te_3$ by about 2 orders of magnitude. It is speculated that some Bi–Te alloys reacted in the bilayer structure of the samples and contributed more thermoelectricity conductivity which made the thin films possess a negative Seebeck coefficient. With increasing annealing temperature, the major phases are the $Bi_{0.5}Sb_{1.5}Te_3$ and Sb–Te phases. The primary charge carrier is a p-type and contributes more thermoelectric conductivity to the thin films which shows positive Seebeck coefficients. The maximum absolute Seebeck coefficient value of 150 μV K^{-1} is gained at a temperature of 300 °C. Electrical conductivity decreases from 6.20×10^2 to 3.80×10^2 S cm^{-1} when the temperature increased from 100 to 150 °C but the electrical conductivity increased when the temperature increased further. The maximum electrical conductivity of 8.36×10^2 S cm^{-1} can be observed when the annealing temperature was 300 °C.

Though the thin film annealed at 300 °C had a better Seebeck coefficient and larger electrical conductivity than others, the crystalline and thermoelectric quality is not satisfied. From the EDS analysis, we find that the thin film is full of Bi, which is one of the reasons that the single phase $Bi_{0.5}Sb_{1.5}Te_3$ cannot be gained. Furthermore, the samples annealed at 300 °C had been prepared with various compositions by fixing the sputtering time of the Bi/Te layer and changing the Sb/Te sputtering time to optimize the thermoelectric performance of bismuth antimony tellurium thin films. Table 1 shows the element content and the thickness as a function of sputtering time. It is found that stoichiometric $Bi_{0.5}Sb_{1.5}Te_3$ thin film is achieved when the Sb/Te sputtering time was 40 min. XRD patterns are shown in Fig. 3. When the Sb/Te sputtering time was 10 min, the peaks corresponded more with the Bi_2Te_3 characteristic peaks. Combining the EDS testing result, the composition of Sb is very low and it can be considered that the thin film has the single Bi_2Te_3 phase. With the increase of Sb/Te sputtering time, the phases related to $Bi_{0.5}Sb_{1.5}Te_3$ can be observed more and more clearly. The $Bi_{0.5}Sb_{1.5}Te_3$ phase is the dominant phase of the films and the Sb/Te sputtering time of films is between 20 min and 30 min. However, there are some peaks related to the Sb–Te and Bi–Te phases which can also be observed. A single $Bi_{0.5}Sb_{1.5}Te_3$ phase with good stoichiometric ratio can be obtained when the Sb/Te sputtering time is 40 min. It indicates that the thin film has better crystalline quality. However, some peaks related to Sb–Te appeared when the sputtering time was increased to 50 min and the $Bi_{0.5}Sb_{1.5}Te_3$

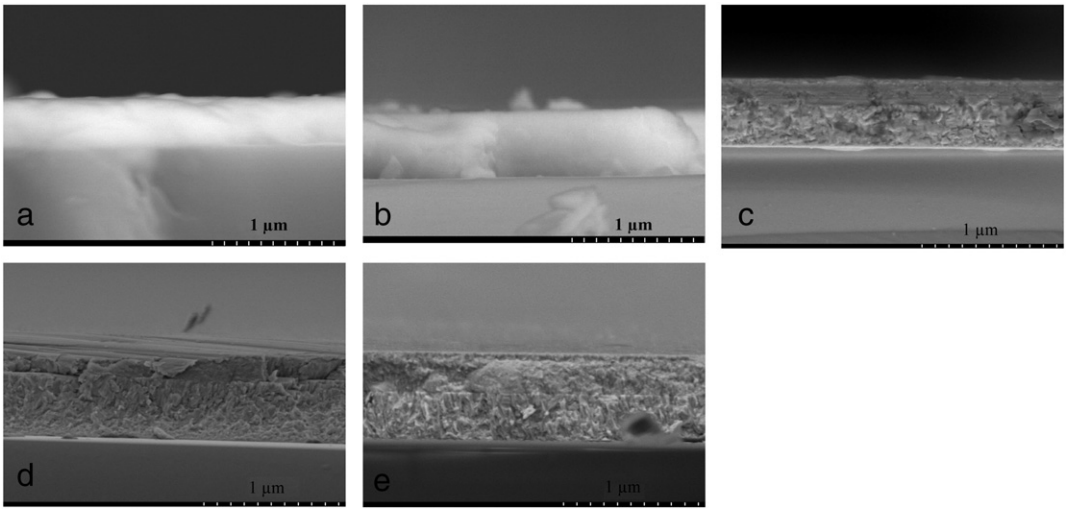

Fig. 4. The SEM cross-section views of the thin films as a function of the Sb/Te sputtering time. 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min.

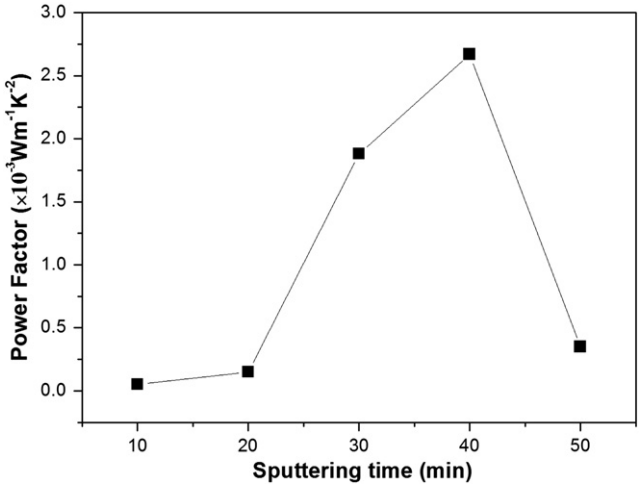

Fig. 6. Plot of power factor obtained as a function of the Sb/Te sputtering time.

phase almost transformed to the Sb–Te phase. The SEM cross-section views of the thin film are showed in Fig. 4. It can be seen that the thin film becomes more and more dense and the grain size increased when the Sb/Te sputtering time increased from 10 min to 40 min. Besides, it can be found that the films are obvious and a "multi-structure" has not been found, indicating that the samples have better crystalline quality. However, when the Sb/Te sputtering time was increased to 50 min, it can be found that the thin film has a "multi-structure" and indicated worse crystalline quality.

Fig. 5 shows the Seebeck coefficient and the electrical conductivity of the thin films as a function of the sputtering time. The power factor (PF), one of the important thermoelectric parameters which determines the performance of the thermoelectric energy conversion is defined as $S^2\sigma$ and has been shown in Fig. 6. The positive Seebeck coefficient suggests that all of thin films are p-type thermoelectric materials. As show in Fig. 5, the Seebeck coefficient increases from 43 μV K^{-1} to 240 μV K^{-1} when the sputtering time increased from 10 min to 40 min. It indicates that the thin film with the single $Bi_{0.5}Sb_{1.5}Te_3$ phase has the highest Seebeck coefficient. With the increase in sputtering time, the electrical conductivity increases from 2.48×10^2 to 8.36×10^2 S cm^{-1} and then decreases to 1.14×10^2 when the sputtering time is above 30 min. The maximum electrical conductivity can be observed with the film of multi-component mixed phases when the sputtering time is 30 min. As shown in Fig. 6, the power factors increase from 0.05×10^{-3} Wm^{-1} K^{-2} to 2.67×10^{-3} Wm^{-1} K^{-2} with increasing sputtering time. However, the PF decreases sharply as the sputtering time increases further. The sample with the Sb/Te sputtering time of 40 min has the maximum power factor value with the highest Seebeck coefficient and a moderate electrical conductivity of 4.64×10^2 S cm^{-1}. From the XRD and EDS analyses, the increase of PF value is due to the improvement of crystalline quality with standard stoichiometric ratio.

4. Conclusions

Bismuth antimony tellurium thin films were synthesized by IBSD via bilayer annealing. p-Type thin film with the single $Bi_{0.5}Sb_{1.5}Te_3$ phase is obtained when the thin film annealed at 300 °C with the Bi/Te and Sb/Te layer sputtering times of 30 min and 40 min, respectively. The thin film with good crystal quality has a maximum power factor of 2.67×10^{-3} Wm^{-1} K^{-2}. Besides, the thin film has a maximum Seebeck coefficient of 240 μV K^{-1} with a moderate electrical conductivity of 4.64×10^2 S cm^{-1}. XRD pattern shows that the thin films have a mixed phase which deteriorates their thermoelectric properties. Obviously, the adjustment of the deposition condition can gain high crystalline quality with enhanced thermoelectric properties of ion beam sputtered bismuth antimony tellurium thin films.

Acknowledgments

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